Effects of silica coating on photocatalytic reactions of anatase titanium dioxide studied by quantitative detection of reactive oxygen species

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ABSTRACT

The effects of silica coating on the photocatalytic properties of anatase titanium dioxide (TiO_2) were studied by quantitative detection of reactive oxygen species under UV-irradiation, because the surface modification with silica has been practically used to suppress the photocatalytic activity in organic supports. For reactive oxygen species such as superoxide radicals ($^\bullet O_2{}^-$), H_2O_2, and OH radicals, the detection methods using MCLA chemiluminescence, lucigenin chemiluminescence, and coumarin fluorescence were employed respectively. By comparing silica-coated TiO_2 with uncoated TiO_2 powders, the amount of H_2O_2 detected under UV irradiation was significantly decreased by silica coating. Thus the silica modification suppressed the release of H_2O_2, which may be the nature of the effect of silica coating for suppressing photocatalytic activity against organic supports.

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1. Introduction

Photocatalytic materials, such as titanium dioxide (TiO_2), are known to have the capability to decompose substances and create hydrophilic surfaces by the action of light energy [1–3]. When photocatalysis is applied to antifouling of house, photocatalytic materials have to be incorporated in a paint, which can be painted on resin sheets or the exterior walls. However, photocatalytic reactions with organic supports often cause chalking in a long term use, that is, the surface of the paint film becomes white powder. Therefore, to decrease this photocatalytic activity, TiO_2 is coated with silica or alumina, which is the method that has been practically used to prevent chalking for a long time [1]. There are many reports which proved that weather resistance of TiO_2 photocatalysts was improved by coating. For example, the increase in the weather resistance was evidenced by measuring the decrease in thickness of paint film [4], and the number of cracks in resin was decreased by using coated TiO_2 powders which increased the weather resistance [5]. On the other hand, though it is not a coated TiO_2, a photocatalyst of TiO_2/SiO_2 complex formed by the sol–gel method has been reported to exhibit a high activity in photocatalytic dye decomposition [6,7]. Another study showed that excellent hydrophilic properties could be obtained for a paint film made by baking a particle mixture of TiO_2 and silica (SiO_2) [8]. Thus, the effect of silica coating on the photocatalytic activity has not been clearly understood yet. Since silica-coated TiO_2 photocatalysts are well-known materials for practical use, it is necessary to explore the effect of coated silica on the photocatalytic reaction from the mechanistic point of view.

Generally the mechanism of photo-induced reaction in TiO_2 photocatalysis proceeds as following mechanism. Photo-absorption in TiO_2 produces conduction band electrons (e^-) and valence band holes (h^+) (Eq. (1)). The conduction band electrons reduce oxygen molecules in air to produce superoxide radicals ($^\bullet O_2{}^-$) (Eq. (2)), which may reduce further to H_2O_2 and OH radicals (Eqs. (3) and (4)). The valence band holes oxidize the reactant when oxidizable organic compounds are adsorbed on the surface (Eq. (5)). In the absence of the reactant, water absorbed on the surface of the TiO_2 is oxidized by holes to produce OH radicals (Eq. (6)) and further to H_2O_2 (Eq. (7)). The produced H_2O_2 may be further oxidized to $^\bullet O_2{}^-$ (Eq. (8)). In the presence of adsorbed reactant, OH radicals may also oxidize it (Eq. (6)). The probability of the direct oxidation by h^+ (Eq. (5)) and the indirect oxidation via $^\bullet OH$ (Eqs. (6) and (5′)) was argued in the recent review article. [9]

$$TiO_2 + h\nu \rightarrow TiO_2(e^- + h^+) \tag{1}$$

$$e^- + O_2 \rightarrow {}^\bullet O_2{}^- \tag{2}$$

$${}^\bullet O_2{}^- + e^- + 2H^+ \rightarrow H_2O_2 \tag{3}$$

$$H_2O_2 + e^- \rightarrow {}^\bullet OH + OH^- \tag{4}$$

$$h^+ + reactant \rightarrow oxidation \tag{5}$$

$$h^+ + H_2O \rightarrow {}^\bullet OH + H^+ \tag{6}$$

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$$\bullet OH + reactant \rightarrow oxidation \tag{5'}$$

$$\bullet OH + h^+ + H_2O \rightarrow H_2O_2 + H^+ \tag{7}$$

$$H_2O_2 + h^+ \rightarrow \bullet O_2^- + 2H^+ \tag{8}$$

These reactive species, holes (h^+) and reactive oxygens ($\bullet O_2^-$, H_2O_2, and $\bullet OH$), are fundamental reaction intermediates involved in photocatalysis and closely related with the photocatalytic activity. To detect these species, the authors used the chemiluminescence and fluorescence-probe methods and ESR spectrometry, and the reaction mechanisms for TiO$_2$ photocatalysts and the TiO$_2$ modified to visible-light response have been analyzed [10–12].

Although silica-coated TiO$_2$ is contained in photocatalytic paints for practical use, the effect of silica treatments has not been quantitatively reported with respect to the reactive species. In our previous study for silica coated TiO$_2$, ESR spectrometry showed that the amount of holes detected at 77 K was not decreased by silica coating. On the decomposition of acetaldehyde and toluene in vapor phase, it was found that the uncoated TiO$_2$ surpassed the silica-coated TiO$_2$ in the initial reaction rate. However, the rate decreased in time, and the silica-coated TiO$_2$ became more active after the reaction proceeded [13]. It was likely that reaction intermediates block the decomposition sites at TiO$_2$ surface. Therefore, in the present study, the effect of silica coating was investigated and discussed by carrying out quantitative detections of reactive oxygen species ($\bullet O_2^-$, H_2O_2, and $\bullet OH$ radical) under UV irradiation in aqueous suspension. As a result, we will elucidate the nature of the silica coating as the effect of suppressing chemical activity.

2. Experiments

2.1. Materials

A sample of silica-coated anatase TiO$_2$ powder was obtained by freeze-drying a silica-coated TiO$_2$ sol (MPT-422, developed by Ishihara Sangyo Ltd.). The fraction of silica in the coated TiO$_2$ was 12 wt.%. For comparison, bare anatase TiO$_2$ powder (ST-01, Ishihara Sangyo Ltd.) was also used. Their specific surface areas were 243 m^2/g and 320 m^2/g, respectively.

2.2. Detection of superoxide radicals ($\bullet O_2^-$)

The amount of superoxide radicals ($\bullet O_2^-$) was measured by the chemiluminescence method with MCLA (Methoxy Cypridina Luciferin Analog, 2-methyl-6-(p-methoxyphenyl)-3,7-dihydroimidazo (1,2-a) pyrazin-3-one hydrochloride, Tokyo Chemical Industry). Fifteen mg of photocatalyst powder was suspended in 3.5 mL of purified water in a quartz cell (1 cm × 1 cm × 4.5 cm) and stirred with a magnetic stirrer in a dark box. The cell containing the suspension was irradiated with UV light using an LED source (LC-L201: wavelength: 365 nm; intensity: 5 mW/cm^2, Hamamatsu Photonics). After the UV irradiation, 50 μL of 0.35 mM MCLA aqueous solution was added to this cell with a micro-syringe, and then the intensity of chemiluminescence caused by $\bullet O_2^-$ was observed with a photon counting system [11]. The $\bullet O_2^-$ concentration was calculated from the accumulated light intensity. The luminol chemiluminescence method [10] was also used to measure the amount of $\bullet O_2^-$ produced by non-modified TiO$_2$, and this value was utilized to calculate the $\bullet O_2^-$ concentration from the intensity of the MCLA chemiluminescence. In the present experiments, the MCLA chemiluminescence method was used, because silica was affected in higher alkaline solution of pH 11.5 where the luminol chemiluminescence method was applied.

2.3. Detection of H$_2$O$_2$

The amount of H$_2$O$_2$ was evaluated by the lucigenin chemiluminescence method [14] with the same experimental setup as MCLA chemiluminescence method. For this measurement, 15 mg of TiO$_2$ was suspended in 3.5 mL aqueous solution adjusted to pH 9 with NaOH. After the UV irradiation, 50 μL of 0.7 mM lucigenin solution was added to observe the chemiluminescence. The chemiluminance intensity recorded as a function of time was integrated over the observation period to evaluate the H$_2$O$_2$ concentration.

A property of the photocatalysts for H$_2$O$_2$ adsorption was evaluated in dark by measuring the concentration of H$_2$O$_2$ in the solution. After adding 10 mM H$_2$O$_2$ solution to the sample solutions with and without TiO$_2$, the lucigenin chemiluminescence method as mentioned above was also used to evaluate the concentration of H$_2$O$_2$. The difference in the detected amounts was applied to calculate the amount of H$_2$O$_2$ adsorbed on the photocatalyst powders.

2.4. Detection of OH radicals

The amount of OH radicals was obtained by the coumarin fluorescence probe method [15]. The same cell and UV source mentioned above were used for this measurement. Fifteen mg of TiO$_2$ was suspended in 3.5 mL of 0.1 mM coumarin aqueous solution. After UV irradiation, 0.5 g of KCl was added to the suspension and then it was stored in dark for one day to precipitate TiO$_2$ powders from the suspension. After that, the fluorescence spectrum of the supernatant solution was measured with a fluorescence spectrophotometer (Model 850, Hitachi). It has been verified that adding KCl did not affect the fluorescence measurement. The fluorescence intensity of this sample was compared with the fluorescence intensity of umbelliferone of known concentration in 0.1 mM coumarin aqueous solution to obtain the OH radical concentration. Since it was shown that 7% of OH radicals can be converted to umbelliferone in 0.1 mM coumarin aqueous solution [15], the same conversion factor was used.

2.5. Effect of H$_2$O$_2$

To examine the presence of H$_2$O$_2$ as the reaction intermediate, in some experiments H$_2$O$_2$ was added in the reaction solution before the UV irradiation. The amounts of superoxide radicals ($\bullet O_2^-$) and OH radicals after the 60 s irradiation were measured by varying the concentration of added H$_2$O$_2$.

3. Results and discussion

3.1. Quantitative detection of oxygen species

Fig. 1 shows the chemiluminescence intensity on the addition of MCLA in the powder suspension after the irradiation of 365 nm LED for 60 s. From the integration of the chemiluminescence intensity over the time detected, the concentration of $\bullet O_2^-$ was calculated and plotted in Fig. 2 as the function of irradiation time. As seen in Fig. 2, the amount of detected $\bullet O_2^-$ was on the order of nM (nanomole dm^{-3}). It is likely that two-electron reduction of oxygen quickly proceeded to produce H$_2$O$_2$ leaving very small amount of $\bullet O_2^-$ as a steady state. (Eqs. (2) and (3)) That is, the $\bullet O_2^-$ generation is a side reaction and not a primary product in the photocatalytic reaction. The $\bullet O_2^-$ generation was larger for silica-coated TiO$_2$ than for uncoated TiO$_2$, suggesting that the coated silica retards the reduction of $\bullet O_2^-$ to H$_2$O$_2$ (Eq. (3)) or accelerates the oxidation of the generated H$_2$O$_2$ to $\bullet O_2^-$ (Eq. (8)). The latter explanation will be denied by the H$_2$O$_2$-addition experiment as described later.

Fig. 3 shows the chemiluminescence intensity observed on the addition of lucigenin in the powder suspension after the irradiation
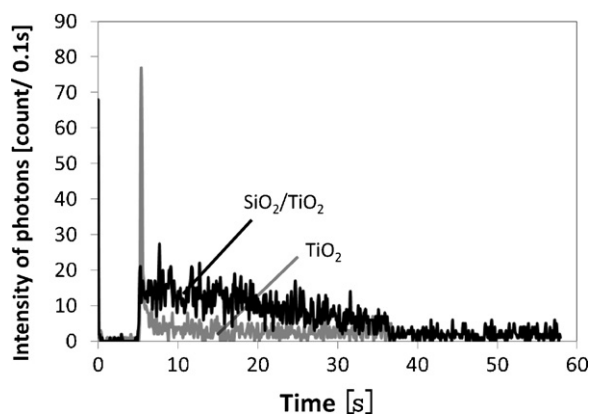
Fig. 1. The intensity of chemiluminescence observed after adding MCLA in the photocatalyst suspensions irradiated for 60 s with UV light, showing the detection of $^\bullet O_2{}^-$. The photocatalysts used were silica-coated (SiO_2/TiO_2) and uncoated TiO_2.
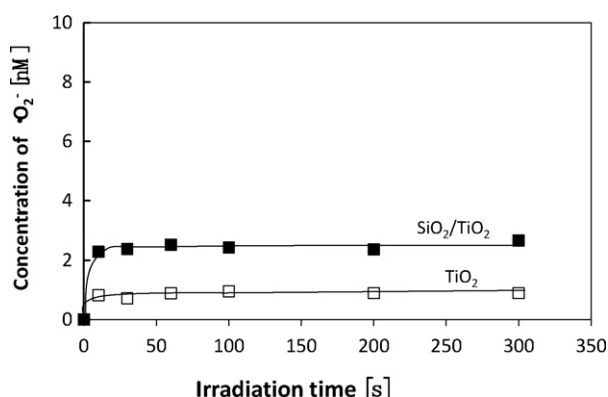

Fig. 2. The $^\bullet O_2{}^-$ concentration calculated from the integration of chemiluminescence intensity representing in Fig. 1 was plotted as a function of the UV-irradiation time for silica-coated (SiO_2/TiO_2) and uncoated TiO_2.

of 365 nm LED for 60 s. Intensity of lucigenin chemiluminescence was integrated and it was converted to the H_2O_2 concentration. In Fig. 4, the concentration of H_2O_2 measured was plotted as the function of the irradiation time. As seen from Fig. 4, the detected amount of H_2O_2 for uncoated TiO_2 is tens of μM (micromole dm^{-3}), far larger than that of $^\bullet O_2{}^-$. The number of photons incident into the reaction solution of 3.5 mL for 60 s can be calculated from the light intensity to be about 300 μM. Then, roughly 10% of photons were used to produce H_2O_2 on the bare TiO_2, indicating a high yield pro-
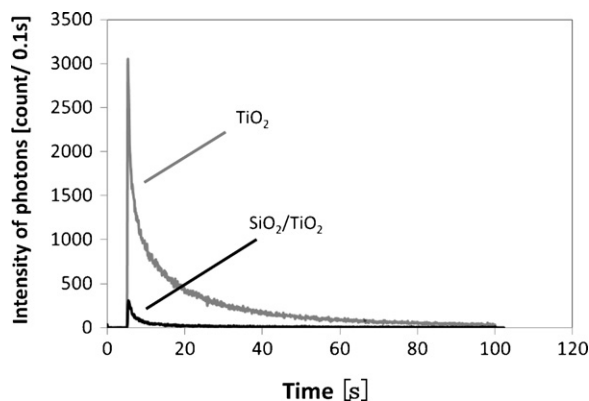

Fig. 3. The intensity of chemiluminescence observed after adding lucigenin in the photocatalyst suspensions irradiated for 60 s with UV light, showing the detection of H_2O_2.
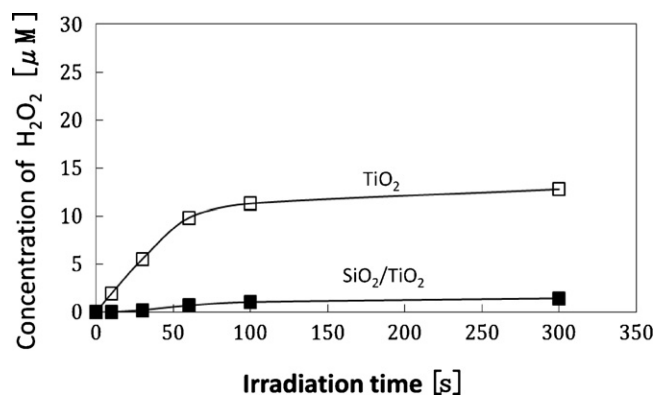

Fig. 4. The H_2O_2 concentration calculated from the integration of chemiluminescence intensity representing in Fig. 3 was plotted as a function of the UV-irradiation time for silica-coated (SiO_2/TiO_2) and uncoated TiO_2.

duction as a first reaction intermediate. On the irradiation longer than 60 s, the amount of H_2O_2 became a steady value. The stop of the increase indicates that the produced H_2O_2 suffered some reaction, likely being oxidized to $^\bullet O_2{}^-$ (Eq. (8)) or reduced to OH radicals (Eq. (4)). On the other hand, in the case of silica-coated TiO_2, H_2O_2 generation was remarkably small compared with the uncoated TiO_2. Silica may have blocked the two-electron reduction of O_2 and two-electron oxidation of water. Also, generated H_2O_2 may have been trapped by coated silica, because the amount detected H_2O_2 was significantly decreased in the first irradiation time up to 30 s.

As for the detection of OH radicals, Fig. 5 shows the fluorescence spectra recorded after 60 s irradiation of powder suspension with coumarin. The peak at 455 nm is assigned to umbelliferone and the small peak at 390 nm to coumarin. The concentration of umbelliferone was calculated from the intensity and converted to the amount of OH radicals. Fig. 6 shows the results of OH radical detection as a function of irradiation time. The growth of OH radical continued for a long term irradiation. This growth feature is different from that for $^\bullet O_2{}^-$ and H_2O_2, where the amounts were leveled off at each steady state as shown in Figs. 2 and 4, respectively. This difference in the growth feature comes from the difference in the detection methods. Namely, coumarin had been introduced before UV irradiation, and umbelliferone was detected as the reaction product with OH radicals. Then the amount of OH radical appeared during the irradiation was accumulated before the detection of umbelliferone concentration. For example, for 60 s irradiation, all OH radicals generated over the 60 s period were detected as the cumulative amount
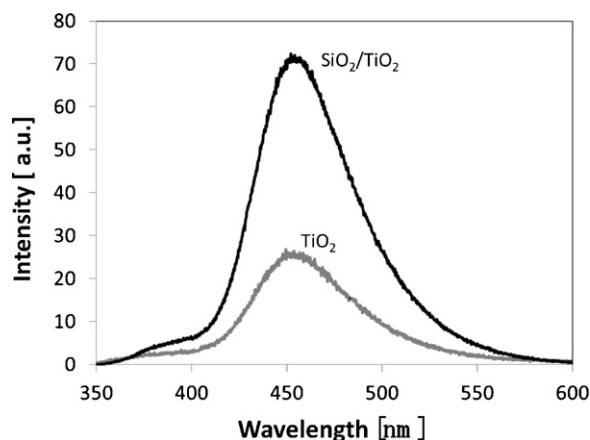

Fig. 5. The fluorescence spectra of 0.1 mM coumarin solution after 300 s irradiation of UV light in the presence of photocatalysts; silica-coated (SiO_2/TiO_2) and uncoated TiO_2.

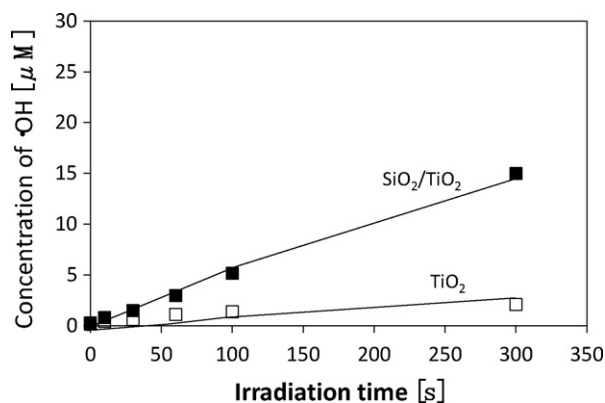**Fig. 6.** The •OH concentration calculated from the increase in the fluorescence peak at 450 nm, which was represented in Fig. 5, is plotted as a function of UV-irradiation time for silica-coated (SiO$_2$/TiO$_2$) and uncoated TiO$_2$.

Fig. 8. Effect of H$_2$O$_2$ concentration on the •O$_2^-$ concentrations detected by the MCLA chemiluminescence method after 60 s irradiation in photocatalyst suspensions.

of generated OH radicals. On the other hand, for the detection of •O$_2^-$ and H$_2$O$_2$, it was after UV irradiation that MCLA and lucigenin were introduced. Therefore, the amounts of •O$_2^-$ and H$_2$O$_2$ were detected at each moment and their amounts were determined by competing reactions between generation and degeneration. As shown in Fig. 6, silica-coated TiO$_2$ surpassed uncoated TiO$_2$ in the formation of OH radicals. It is most likely that the coated silica blocked OH radicals from being dimerized or oxidized into H$_2$O$_2$, causing them to remain OH radicals.

3.2. Effects of H$_2$O$_2$ on the photocatalytic mechanism

At first, the number of H$_2$O$_2$ molecules adsorbed to each type of TiO$_2$ was examined. Fig. 7 shows the surface density of adsorbed H$_2$O$_2$ calculated from the decrease of the H$_2$O$_2$ concentration in solution and BET specific surface area of the powders. As seen from Fig. 7, silica-coated TiO$_2$ surpasses uncoated TiO$_2$ in the number of adsorbed molecules. This observation clearly shows that silica at the surface adsorbs H$_2$O$_2$ molecules more preferably than TiO$_2$ surface, but the difference is not much to explain the large difference in the amount of H$_2$O$_2$ detected (Fig. 4).

Since the formation of H$_2$O$_2$ was large, production of •O$_2^-$ and •OH radicals from H$_2$O$_2$ were examined by adding H$_2$O$_2$. Fig. 8 shows the amount of detected •O$_2^-$ as a function of the added H$_2$O$_2$ concentration. The addition of H$_2$O$_2$ in the reaction system increased the •O$_2^-$ for both silica-coated and uncoated TiO$_2$, indicating that H$_2$O$_2$ is oxidized to produce •O$_2^-$ (Eq. (8)). Though the oxidation path of H$_2$O$_2$ was seen, this is a side reaction, because
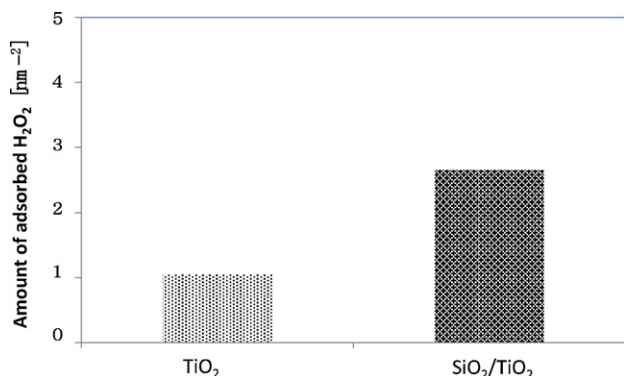
the generation of •O$_2^-$ was stopped at a small amount of 60 nM. For silica-coated TiO$_2$, the amount of •O$_2^-$ increased with smaller amount of H$_2$O$_2$ than that for uncoated TiO$_2$. This observation suggests that the silica coating increased H$_2$O$_2$ adsorption and then the oxidation rate was increased to produce •O$_2^-$.

Fig. 9 shows the amount of OH radicals as a function of the amount of H$_2$O$_2$ added. The addition of H$_2$O$_2$ significantly decreased the •OH formation for both silica-coated and uncoated TiO$_2$. The addition of H$_2$O$_2$ should increase the •OH production, if OH radical were mainly produced from O$_2$ by three-electron reduction via H$_2$O$_2$ (Eqs. (2) and (4)). However, Fig. 9 showed that OH radical is not produced from H$_2$O$_2$. Therefore, for the anatase TiO$_2$ in this study, oxidation of water is the dominant contribution to the •OH production (Eq. (6)) and it becomes H$_2$O$_2$. In other words, OH radicals were produced as the byproduct in the process of two-electron oxidation of water into H$_2$O$_2$ (Eqs. (6) and (7)). The reason for the decrease in the detected OH radicals with the addition of H$_2$O$_2$ is likely that the H$_2$O$_2$ is easily oxidized compared with the oxidation of water, because one electron oxidation potentials for H$_2$O$_2$ and H$_2$O at pH 0 are E (•HO$_2$ + H$^+$/H$_2$O$_2$) = +1.48 V and E (•OH + H$^+$/H$_2$O) = +2.7 V (vs. NHE), respectively [12]. The addition of a small amount of H$_2$O$_2$ (0.1 mM) caused a larger decrease in OH radical production for silica-modified TiO$_2$, suggesting that the H$_2$O$_2$ adsorption is exceptionally strong for coated silica.

Fig. 10 schematically illustrates the generation mechanism of reactive oxygen species on the surface of TiO$_2$ under UV irradia-

Fig. 7. The amount of H$_2$O$_2$ adsorbed on uncoated titanium dioxide (TiO$_2$) and silica-coated titanium dioxide (SiO$_2$/TiO$_2$) calculated from the decrease of the concentration of 10 mM solution in dark.

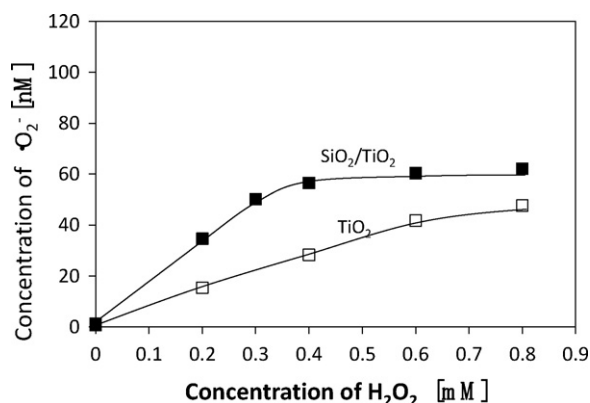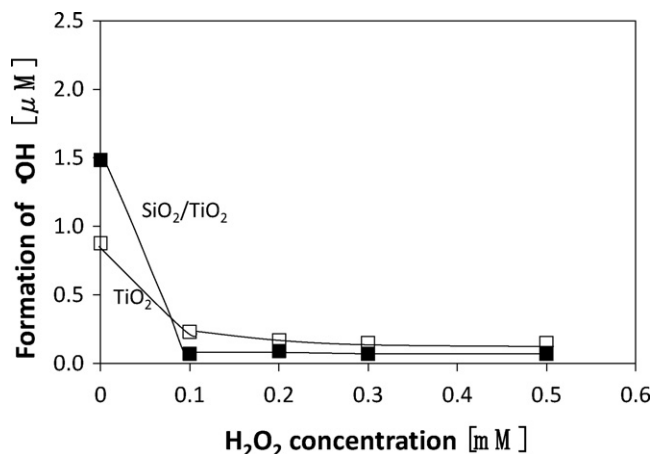**Fig. 9.** Effect of H$_2$O$_2$ concentration on the •OH concentration measured by the coumarin fluorescence probe method after 60 s irradiation in photocatalyst suspension.
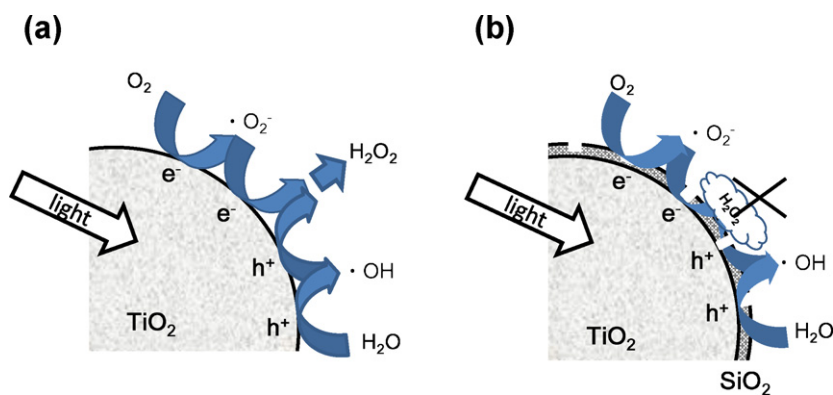
Fig. 10. Plausible reaction scheme for the active oxygen species formation at the irradiated TiO_2 surface. (a) uncoated TiO_2, (b) silica-coated TiO_2.

tion. In the absence of organic reactants, UV-irradiation on anatase TiO_2 produces H_2O_2 from both two-electron oxidation of water and two-electron reduction of O_2. As byproducts of each two-electron reaction, small amounts of $^\bullet OH$ and $^\bullet O_2{}^-$ radicals may be produced. The $^\bullet O_2{}^-$ as a product of the O_2 reduction may also be produced from the oxidation of H_2O_2. Since silica coating largely decreased the H_2O_2 formation, SiO_2 may inhibit two-electron reduction of oxygen and two-electron oxidation of water, and then, the increases in the one electron reaction intermediates, $^\bullet O_2{}^-$ and $^\bullet OH$ radicals, were observed, respectively. Therefore, the fact that silica coating on TiO_2 improves the weather resistance of resin, or organic support, is explained by the small release of H_2O_2 by the coating.

4. Conclusions

The effects of coating with silica on photocatalytic properties of TiO_2 were studied by quantitative detection of reactive oxygen species ($^\bullet O_2{}^-$, H_2O_2, and OH radical) under UV irradiation using suspensions of silica-coated and uncoated TiO_2. The experiments of H_2O_2 addition revealed that H_2O_2 was produced from two-electron reduction of O_2 (Eqs. (2) and (3)) and the oxidation of water (Eqs. (6) and (7)), and that a small amount of $^\bullet O_2{}^-$ and $^\bullet OH$ radicals were formed as intermediate byproducts of the two-electron reduction and oxidation reactions. By comparing with uncoated TiO_2, the amount of H_2O_2 detected became significantly smaller by silica-coating, indicating that the coated silica prevent the production of

H_2O_2. The well-known effect of silica coating on the suppression of the photocatalytic activity of anatase TiO_2 to organic supports is likely caused by the decrease of H_2O_2 formation. In other words, silica modification causes a decrease in H_2O_2 release to prevent TiO_2 from the decomposition of the binder resins.

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